ORGANIC LETTERS

2011
Vol. 13, No. 8
1936–1939

Thiadiazoloquinoxalines: Tuning Physical Properties through Smart Synthesis

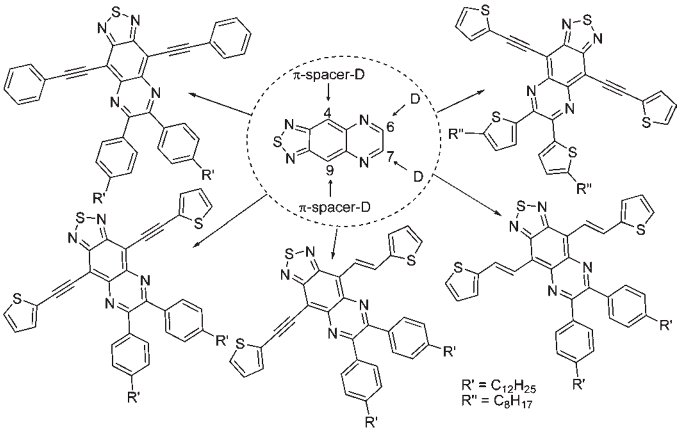
Timea Dallos, Manuel Hamburger, and Martin Baumgarten*

Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

martin.baumgarten@mpip-mainz.mpg.de

Received January 26, 2011

ABSTRACT



The synthesis of π-conjugated acceptors based on thiadiazoloquinoxaline (TQ) derivatives is described. Apart from reporting on the functionalization of the TQ core, the influence of the substituents was studied by UV−vis absorption and emission spectroscopy, cyclic voltammetry measurements, and DFT calculations. By changing the donor as well as the π-spacer, a fine-tuning of the photo- and electrochemical properties was achieved.

Organic π-conjugated molecules and polymers are versatile materials for the application in light emitting diodes,[1] photovoltaic cells,[2] field effect transistors,[3] and nonlinear optics[4]. Distinct synthetic design in these systems allows the tailoring of the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).[5] The HOMO−LUMO gap determines the optical and electrochemical behavior of π-conjugated systems therefore their applicability in electronic devices. An effective synthetic strategy to decrease the HOMO−LUMO gap involves the alternation of electron-donating (D) and electron-accepting (A) moieties, within the engineered molecular backbone, thus implicitly increasing the conjugation length.[6] To maximize the effective π-conjugation length, steric interactions between adjacent units needs to be minimized.[7] Hence, within D−A−D type molecules, the introduction of π-spacers such as olefinic or acetylenic π-spacers enables the generation of structures with

---

(1) (a) Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009**, *109*, 897. (b) Saleh, M.; Baumgarten, M.; Mavrinskiy, A.; Schäfer, T.; Müllen, K. *Macromolecules* **2010**, *43*, 137.

(2) (a) Inganäs, O.; Zhang, F.; Andersson, M. R. *Acc. Chem. Res.* **2009**, *42*, 1731. (b) Li, C.; Liu, M.; Pschirer, N. G.; Baumgarten, M.; Müllen, K. *Chem. Rev.* **2010**, *18*, 4619. (c) Silvestri, F.; Marrocchi, A. *Int. J. Mol. Sci.* **2010**, *11*, 1471.

(3) (a) Gao, P.; Beckmann, D.; Tsao, H. N.; Feng, X. L.; Enkelmann, V.; Baumgarten, M.; Pisula, W.; Müllen, K. *Adv. Mater.* **2010**, *21*, 213. (b) Arias, A. C.; MacKenzie, J. D.; McCulloch, I.; Rivnay, J.; Salleo, A. *Chem. Rev.* **2010**, *110*, 3.

(4) (a) Parthasarathy, A.; Ahn, H.-Y.; Belfield, K. D.; Schanze, K. S. *ACS Appl. Mater. Interfaces* **2010**, *2*, 2744. (b) Wu, P. L.; Feng, X. J.; Tam, H. L.; Wong, M. S.; Cheah, K. W. *J. Am. Chem. Soc.* **2009**, *131*, 886.

(5) (a) Skotheim, T. A.; Reynolds., J., Eds. *Conjugated Polymers*; CRC Press, Taylor and Francis Group: Tampa, FL, 2006. (b) Mishra, A.; Ma, C.-Q.; Bäuerle, P. *Chem. Rev.* **2009**, *109*, 1141. (c) Welch, G.; Coffin, R.; Peet, J.; Bazan, G. C. *J. Am. Chem. Soc.* **2009**, *131*, 10802. (d) Ajayaghosh, A. *Chem. Soc. Rev.* **2003**, *32*, 181.

(6) (a) Havinga, E. E.; ten Hoeve, W.; Wynberg, H. *Polym. Bull.* **1992**, *29*, 119. (b) Havinga, E. E.; ten Hoeve, W.; Wynberg, H. *Synth. Met.* **1993**, *55*, 299.

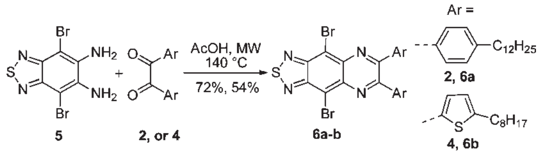
(7) (a) Bredas, J. L.; Chance, R. R.; Baughman, R. H.; Silbey, R. *J. Chem. Phys.* **1982**, *76*, 3673. (b) Swager, T. M.; Gil, C. J.; Wrighton, M. S. *J. Phys. Chem.* **1995**, *99*, 4886.

(8) (a) Schenning, A. P. H. J.; Tsipis, A. C.; Meskers, S. C. J.; Beljonne, D.; Meijer, E. W.; Bredas, J. L. *Chem. Mater.* **2002**, *14*, 1362. (b) Silvestri, F.; Marrocchi, A.; Seri, M.; Choongik, K.; Marks, T. J.; Facchetti, A.; Taticchi, A. *J. Am. Chem. Soc.* **2010**, *132*, 6108.

10.1021/ol200250e

increased conjugation, while keeping steric constraints at a minimum.[8] The [1,2,5]thiadiazolo[3,4]quinoxaline (TQ) molecule is an *o*-quinoid acceptor unit featuring outstanding electron affinity and has been used in the construction of low band gap semiconducting polymers.[9] So far, TQ derivatives were reported in conjugation with neighboring thiophene units at positions 4 and 9.[10]

Scheme 1. Synthesis of 4,9-Dibromo-6,7 bis(aryl)-[1,2,5]-thiadiazolo[3,4-*g*]quinoxaline

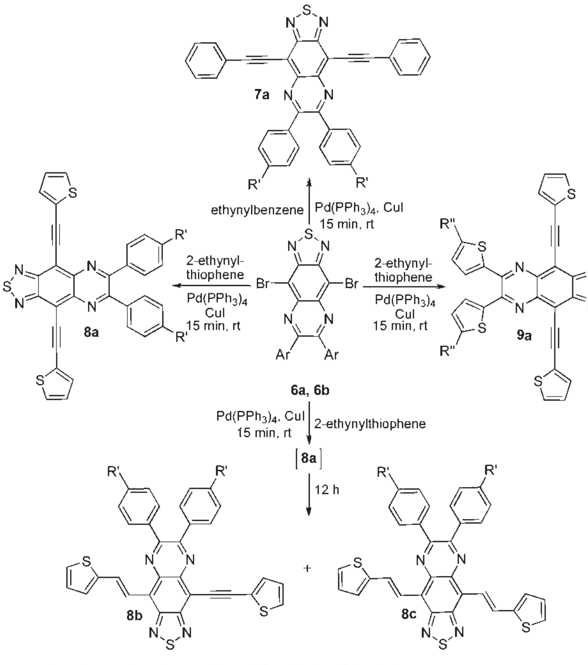


Herein, we report the synthesis and characterization of new TQ oligomers with neighboring ethynyl and vinyl spacers. The changes in the optical and electrochemical behavior originating from the difference in the donor strength of the substituents at positions 6 and 7 on the TQ unit, as well as in the nature of π-spacers (ethynyl vs. vinyl) in the co-oligomers (at positions 4 and 9), are reported (Figure S1, Supporting Information, SI).

Diketones **2** and **4** were obtained from the commercially available dodecylbenzene or octylthiophene under Friedel–Crafts reaction conditions in 56% and 72% yield, respectively.[11] The condensation of **5**[12,9b] with diketone **2** or **4** was conducted in acetic acid (AcOH), under microwave (MW) irradiation (Scheme 1). Compounds **6a** and **6b** were isolated as orange (**6a**, 72% yield) and red (**6b**, 54% yield) precipitates.

Performing the well-established one-pot consecutive Sonogashira–Hagihara[13] cross-coupling reaction between **6a**,**b** and the corresponding aromatic terminal alkyne led to the formation of **7**–**9a** (77–82% yield) in only 15 min (Scheme 2). Trying to increase the yield of **8a** by extending the reaction time of **6a** and 2-ethynylthiophene resulted in the formation of **8b** and **8c**, respectively. The highest yields for **8b** (16% yield) and **8c** (12% yield) were obtained after 12 h, whereas neither **6b** nor **8a** was left in the reaction mixture. The hydrogenation of the alkyne **8a** indicated that, after the coupling reaction was completed, the palladium catalyst acted as a hydrogen-transfer catalyst, reducing the triple bond. The hydrogen source might be the diisopropylammonium salt, resulting from the deprotonation of the terminal acetylene. The presumed Pd-catalyzed hydrogenation might be facilitated by the strong electron-withdrawing nature of the TQ core.[14]

Scheme 2. Synthesis of TQ Derivatives **7a**, **8a**–**c**, and **9a**



Ar = dodecylphenyl, 5-octylthienyl; R' = $C_{12}H_{25}$; R'' = C_8H_{17}

First, the influcence of the substituents directly connected to the TQ core, at positions 6 and 7, was evaluated (Table 1). Compound **6a**, carrying phenyl moieties, showed an absorption maximum at 440 nm and an emission maximum at 546 nm (Figure S2, SI). Replacing the phenyl substituents by thiophene (**6b**) enhanced the D–A interactions, lowering the optical energy gap (E_{op}). This was reflected in red shifts of the absoption and emission maxima in solution. To determine the electrochemical properties of the compounds, cyclic voltammetry (CV) experiments were performed and the first reduction peak potentials (E_{Red}) relative to ferrocene were measured (Figure S3, SI). The CV measurements revealed that both compounds presented similar E_{LUMO} (Table 1) suggesting that, by the introduction of stronger donor units at positions 6 and 7, the high electron affinity of the molecule was preserved.

Second, the photophysical properties of **7a**, **8a**, and **9a** (Figure 1, Table 1) could be tuned by varying the donor strength connected via acetylenic spacers at the 4 and 9 positions.

---

(9) (a) Kitamura, C.; Tanaka, S.; Yamashita, Y. *Chem. Mater.* **1996**, *8*, 570. (b) Cai, T.; Zhou, Y.; Wang, E.; Hellström, S.; Zhang, F.; Xu, S.; Inganäs, O.; Andersson, M. R. *Sol. Energy Mater. Sol. Cells* **2010**, *94*, 1275.

(10) (a) Wang, E.; Hou, L.; Wang, Z.; Hellström, S.; Mammo, W.; Zhang, F.; Inganäs, O.; Andersson, M. R. *Org. Lett.* **2010**, *12*, 4470. (b) Li, H.; Tam, T. L.; Lam, Y. M.; Mhaisalkar, S. G.; Grimsdale, A. C. *Org. Lett.* **2011**, *13*, 46.

(11) Belen'kii, L. I.; Shirinyan, V. Z.; Gromova, G. P.; Kolotaev, A. V.; Strelenko, Y. A.; Tandura, S. N.; Shumskii, A. N.; Krayushkin, M. M. *Chem. Heterocycl. Compd.* **2003**, *39*, 1570.

(12) (a) Tsubata, Y.; Suzuki, T.; Yamashita, Y.; Mukai, T.; Miyashi, T. *Heterocycles* **1992**, *33*, 337. (b) Tam, T. L.; Li, H.; Wei, F.; Tan, K. J.; Kloc, C.; Lam, Y. M.; Mhaisalkar, S. G.; Grimsdale, A. C. *Org. Lett.* **2010**, *12*, 3340.

(13) Tohda, Y.; Sonogashira, K.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467.

(14) (a) Raebiger, J. W.; Miedaner, A.; Curtis, C. J.; Miller, S. M.; Anderson, O. P.; DuBois, D. L. *J. Am. Chem. Soc.* **2004**, *126*, 5502. (b) Hierso, J. C.; Picquet, M.; Cattey, H.; Meunier, P. *Synlett* **2006**, *18*, 3005.

Table 1. Photophysical and Electrochemical Properties of **6a**,**b**, **7a**, **8a**−**c**, and **9a**

compd	λ_{abs}/nm (log ε)[a]	λ_{em}/nm[a] (Φ/%[b])	λ_{abs}/nm (λ_{em}/nm) film[c]	E_{op}/eV[a]	E_{Red}/V[d]	E_{LUMO}/eV[e]	E_{HOMO}/eV[f]	E_{calc}/eV[g]
6a	440 (4.33)	546 (−)		2.30	−0.630	−3.79	−6.09	2.65
6b	304 (4.50), 356 (4.33), 495 (4.38)	583 (−)		2.17	−0.621	−3.80	−5.97	2.56
7a	304 (4.68), 460 (4.24), 556 (4.20)	634 (79)	311, 466, 564, 607 (645)	1.98	−0.622	−3.79	−5.77	2.02
8a	352 (4.55), 464 (4.10),586 (4.17)	673 (30)	312, 595 (695)	1.86	−0.611	−3.80	−5.66	1.89
8b	360 (4.68), 628 (4.25)	721 (6)	366, 630, 688 (752)	1.73	−0.662	−3.75	−5.48	1.79
8c	370 (4.61), 648 (4.11)	745 (1)	372, 675, 745 (798)	1.64	−0.707	−3.70	−5.34	1.69
9a	361 (4.64), 556 (4.38), 640 (4.18)	682 (13)	355, 555, 646 (701)	1.78	−0.592	−3.83	−5.62	1.86

[a] In chloroform (1×10^5 M). [b] In toluene estimated by using the comparative method with cresyl violet as standard fluorophore (Φ = 67% in methanol). [c] Spincoated on a glass substrate from a 10 mg/mL toluene solution (thikness 120 nm). [d] 0.1 mol·dm^{-3} of n-Bu$_4$NPF$_6$, in THF, Pt electrode, scan rate 50 mV s^{-1}. [e] Calculated $E_{LUMO} = -(E_{Red,onset} - E^{(1/2)}{}_{Fc^+/Fc} + 4.8)$ eV. [f] Calculated from $E_{opt} - E_{LUMO}$. [g] DFT quantum mechanical calculations (B3LYP/6-31G*).

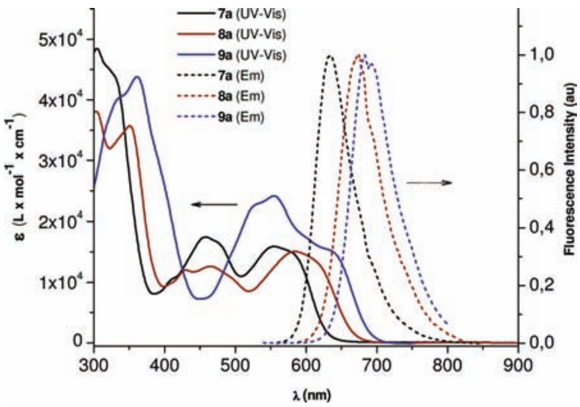


Figure 1. UV−vis absorption (solid line) and emission (dashed line) spectra of the compounds **7**−**9a** in chloroform.

All three compounds displayed strong absorption in chloroform between 300 and 400 nm. In addition, two bands were found around 450 and 556 nm for **7a** and around 450 and 586 nm for **8a**, respectively. These two additional absorption bands originate from the orthogonal extension of the conjugation.[15] In this series, compound **9a**, bearing only thiophene substituents, showed the lowest E_{op}. The long wavelength absorption was extended up to 690 nm with a maximum at 556 nm (shoulder at 640 nm). Moreover, a weak solvatochromism ($\Delta\lambda_{max}$) between hexane and chloroform solutions was observed in this case ($\Delta\lambda_{max}$ = 13 nm) (Figure S6, SI). Interestingly, as the solvent polarity goes beyond chloroform, **9a** exhibited a negative solvatochromism ($\Delta\lambda_{max}$ from chloroform to acetone was −15 nm). Such a phenomenon was previously reported[16] and was ascribed to the back electron transfer from the acceptor side to the donor side in polar solvents. All three compounds revealed red luminescence. In the series **7a**, **8a**, and **9a**, the quantum yield[17] decreased from 79% (**7a**) to 30% (**8a**) and to 13% (**9a**). The introduction of thiophene units in the molecule significantly reduced the fluorescence quantum yield due to efficient intersystem crossing induced by the heavy atom effect of sulfur.[18] Additionally, in all three cases, the emission spectra displayed a strong solvent dependence (Figures S4−S6, SI). Bathochromic shifts of 20 (**7a**), 31 (**8a**), and 23 nm (**9a**) were registered from hexane to chloroform, evidencing a more polar molecular structure in the excited state than in the ground state. Hence, an efficient charge transfer from the donor to the electron-deficient TQ core occurs. The photophysical behavior in film was examined as well (Figures S4−S6, SI). The broadening of the low-energy absorption bands together with the red shift of the emission maxima propounded an effective π−π stacking in the solid state. According to the CV investigations, all three compounds exhibited 3-electron reduction reactions characteristic for the TQ core, out of which the first was found to be typically Nernstian and the other two were quasireversible (Figure S7, SI, Table 1). The E_{LUMO} levels, as determined from the E_{Red}, showed a slight decrease in the series **7**−**9a**. Furthermore, considering the direct correlation between the LUMO levels and the E_{op}, the E_{HOMO} levels were calculated and listed in Tabel 1. The E_{HOMO} levels were most affected by the structural modification. The increasing number of thiophene units (donor strength) increased the E_{HOMO} levels and thus lowered the band gap.

Finally, the photophysical and electrochemical impact of the π-spacer (triple bond vs double bond) in the series **8a**, **8b**, and **8c**, was evaluated (Table 1).

The absorption spectra in chloroform revealed two main absorption bands for **8b** and **8c** (Figure 2). The first intense band appeared around 365 nm with a broad shoulder at 435 nm and a second appeared at 628 (**8b**) and 648 nm (**8c**), respectively. The systematic replacement of the ethynyl units by a vinyl π-spacer gave rise to intense red shifts of the lower energy absorption and fluorescence maxima. Furthermore, the better structural organization in film is

---

(15) Boixel, J.; Blart, E.; Pellegrin, Y.; Odobel, F.; Perin, N.; Chiorboli, C.; Fracasso, S.; Ravaglia, M.; Scandola, F. *Chem.—Eur. J.* **2010**, *16*, 9140.

(16) Davies, J. A.; Elangovan, A.; Sullivan, P. A.; Olbricht, B. C.; Bale, D. H.; Ewy, T. R.; Isborn, C. M.; Eichinger, B. E.; Robinson, B. H.; Reid, P. J.; Li, X.; Dalton, L. R. *J. Am. Chem. Soc.* **2008**, *130*, 10565.

(17) (a) Isak, S. J.; Eyring, E., M. *J. Phys. Chem.* **1992**, *96*, 1738. (b) Williams, A.; Winfield, S. A.; Miller, J. N. *Analyst* **1983**, *108*, 1067.

(18) de Melo, J. S.; Burrows, H. D.; Svensson, M.; Andersson, M. R.; Monkman, A. P. *J. Chem. Phys.* **2003**, *118*, 1550.

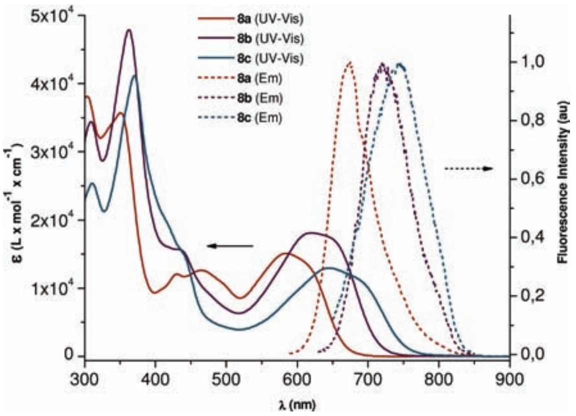


Figure 2. UV−vis absorption (solid line) and emission (dashed line) spectra of the compounds **8a**−**c** in chloroform.

illustrated by the significant red shift of both absorption and emission in film relative to solution (Figure S8, SI). The E_{LUMO} levels were determined from the reduction potentials and listed in Table 1 (Figure S9, SI). The increase of the E_{LUMO} could be assigned to the stronger electron-donating property of the vinyl spacer compared to the ethynyl spacer. Moreover, the E_{HOMO} levels derived from the optical band gap were increased with the introduction of vinyl spacers.

Quantum mechanical calculations by density functional theory (DFT), using B3LYP functional with 6-31G* basis set, were employed to establish the geometry and electronic structure of the presented molecules (Figure S10, SI). The calculations revealed that in all compounds the LUMO orbitals are localized on the TQ core and the HOMO levels reside along the conjugated backbone. Although the calculated energy levels were higher than the ones determined experimentally, the same trend was ascertained. The predicted energy gaps were in good agreement with the optical ones (Table 1). The results of the DFT calculations supported the experimently determined observations according to which, employing ethynyl spacers slightly decreased the LUMO energy levels of the compounds (see **7a**, **8a**, and **9a**), while vinyl spacers increased both HOMO and LUMO levels. In total, however, it led to lower energy gaps (see **8a**, **8b**, and **8c**) (Figures S10 and S11, SI).

In conclusion, by attaching a strong donor at positions 6 and 7 to the TQ core its high electron affinity was not altered, but the energy gap was significantly reduced. Furthermore, the photophysical and electrochemical properties of these new TQ based molecules were tunable by the nature of the donor moiety and π-spacer at positions 4 and 9. By extending the conjugation through D-acetylene spacer low-energy absorbing and red-emitting molecules were accessible having low-lying LUMO energy levels. Additionally, their good solubility in common organic solvents and good thermal stability (Figure S12, SI) render these systems particularly attractive for organic photovoltaics or field effect transistors. Furthermore, the ethynyl spacer could be easily reduced to a vinyl spacer, in a one-pot fashion, by increased reaction time. These changes led to an extended intramolecular conjugation for fine-tuning of the photophysical and electrochemical properties.

Acknowledgment. Financial support by the European Union within the SolarNtype (MRTN-CT-2006-03553) project is gratefully acknowledged. We also thank Dr. Simon Stelzig (Max Plank Instutute for Polymer Research, Mainz) and Dr. Giorgio Zoppellaro (Department of Molecular Biosciences, University of Oslo) for fruitful discussions. We are indebted to Dr. Norbert Hanold (Institute of Organic Chemistry, University of Mainz) for carrying out the ESI measurements.

Supporting Information Available. Synthetic procedures, NMR, MALDI-TOF, ESI, IR, photophysical, and electrochemical data, computational details, and MW reaction profiles. This material is available free of charge via the Internet at http://pubs.acs.org.